EXHIBIT 68

Sorption behaviour of perfluoroalkyl substances in soils

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HIGHLIGHTS

- Sorption isotherms of PFOS, PFOA and PFBS in soils are linear.
- Sorption affinity of PFASs increases with the hydrophobicity of the compound.
- Sorption reversibility decreases when the hydrophobicity of the PFAS increases.
- Sorption K_d correlates to the soil organic matter content.
- K_{OC} values are obtained from the K_d-organic matter correlation.

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ABSTRACT

The sorption behaviour of three perfluoroalkyl substances (PFASs), perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutane sulfonic acid (PFBS), was studied in six soils with contrasting characteristics, especially in the organic carbon content. Sorption isotherms were obtained by equilibrating the soil samples with 0.01 mol L^{-1} $CaCl_2$ solutions spiked with increasing concentrations of the target PFAS. The sorption reversibility of PFASs was also tested for some of the samples. Liquid chromatography coupled to tandem mass spectrometry was used to quantify the target PFASs in the solutions. Both the Freundlich and linear models were appropriate to describe the sorption behaviour of PFASs in soils, and enabled us to derive solid–liquid distribution coefficients (K_d) for each compound in each soil. K_d values increased from 19 to 295 mL g^{-1} for PFOS, from 2.2 to 38 mL g^{-1} for PFOA and from 0.4 to 6.8 mL g^{-1} for PFBS, and were positively correlated with the organic carbon content of the soil. K_{OC} values obtained from the correlations were 710, 96 and 17 mL g^{-1} for PFOS, PFOA and PFBS, respectively. Whereas K_d values decreased in the sequence PFOS > PFOA > PFBS, desorption yields were lower than 13% for PFOS, from 24 to 58% for PFOA, and from 32 to 60% for PFBS. This shows that the physicochemical characteristics of PFASs, basically their hydrophobicity, controlled their sorption behaviour in soils, with PFOS being the most irreversibly sorbed PFAS.

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1. Introduction

Perfluoroalkyl substances (PFASs) are characterised by a fully fluorinated hydrophobic alkyl chain of varying length, attached to different hydrophilic groups, such as sulfonate or carboxyl. Due to their exceptional surface-active properties, these compounds have been widely used in many applications such as stain- and water-resistant textiles, food packaging, fire-extinguishing formulations, pesticides, paints, personal care products and surfactant agents (Lau et al., 2007). Strong C–F bonds make PFASs extremely resistant to hydrolysis and to thermal, microbiological and photolytic degradation. As a consequence, they are ubiquitous in diverse environmental matrices, including water

(Taniyasu et al., 2003; Ahrens et al., 2009), sewage sludge (Yoo et al., 2009; Sun et al., 2011), soils (Strynar et al., 2012; Wang et al., 2013) and sediments (Bao et al., 2010; Yang et al., 2011). In recent years, PFASs have come to public and scientific attention because of their high bioaccumulation, extreme persistence, and toxic properties, such as endocrine disrupting activity and carcinogenesis (Kannan, 2011).

Of all the PFASs, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) show the highest accumulation in the environment (Ellis et al., 2004). These compounds have been directly released or generated by the microbial degradation of other PFAS precursors (Paul et al., 2009). In 2009, PFOS and its salts were added to the Stockholm Convention's list of persistent organic pollutants, and hence their production and use in most applications was prohibited in the EU (UNEP, 2009). Recently, perfluorobutane sulfonic acid (PFBS) has been commercialised as a homologous compound of PFOS in a

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variety of applications (OECD, 2006). PFBS also has a sulfonate hydrophilic group, but a shorter carbon chain, which makes it less bioaccumulative than PFOS (Newsted et al., 2008).

Data on the concentrations of PFASs in soils are scarce in the literature. PFASs were found at ng g^{-1} levels in ten soil samples from several countries (Japan, Mexico and the USA), with the highest concentrations found for PFOS and PFOA, which were 10 and 30 ng g^{-1}, respectively (Strynar et al., 2012). Li et al. (2010) reported similar concentration levels of PFOS and PFOA in soils from Shanghai, China, directly related to the manufacturing and usage of perfluoro-containing products, which is still permitted in this country (Wang et al., 2010; Wang et al., 2013). However, not only the total amount of PFASs in soils, but also their distribution between the solid phase and the soil solution is of great importance, as it influences their environmental fate. Whereas some studies have reported sorption parameters such as the solid–liquid distribution coefficient (K_d) of PFOS and PFOA in sediments, as appear in the review of Zareitalabad et al. (2013), to date, only limited data are available for sorption experiments carried out in mineral soils (Enevoldsen and Juhler, 2010; Chen et al., 2013) and pure phases of soils (Johnson et al., 2007). In these studies, K_d values varied by up to two orders of magnitude. This suggests that various factors influence the sorption pattern of PFASs in soils, and the most important appears to be soil organic carbon. Nevertheless, there is a lack of information on PFASs in soils with a relatively high amount of organic matter as well as on the reversibility of the sorption process.

In order to better understand the distribution of PFASs in soils, particularly soils with a significant amount of organic matter, we evaluated the sorption behaviour of PFOS, PFOA and PFBS, which have different physicochemical properties, in six soil samples with a broad range of organic carbon content. Sorption isotherms were obtained for the target PFASs in a wide range of concentrations, and K_d values were derived from fitting the isotherms to appropriate simple models (Freundlich and linear). The main soil characteristics, as well as the physicochemical properties of PFASs, were considered to explain their sorption mechanisms. Furthermore, the sorption reversibility of each compound was determined and compared.

2. Experimental part

2.1. Reagents and standards

Milli-Q double deionised water (18.2 MΩ cm^{-1}) was obtained from a USF PureLaB Plus water purification system (Spain). Water, ammonium acetate and acetonitrile, all of them gradient grade for liquid chromatography, were supplied by Merck (Germany). Analytical standards of perfluorooctanesulfonate (PFOS, potassium salt, 98%) and perfluorooctanoic acid (PFOA, 99.2%) were purchased from Sigma-Aldrich (Germany), and perfluorobutanesulfonate (PFBS, tetrabutylammonium salt, 98%) was purchased from Sigma-Aldrich (Switzerland). The main physicochemical properties of the PFASs selected for this study are shown in Table 1 (Deng et al., 2012). Of the three PFASs, PFBS is the most soluble in water and is more likely to be transported into aqueous environments than PFOA and PFOS, which are less soluble in water. Moreover, the three PFASs have very low pK_a values ($pK_a < 0.1$), and thus all of them will be dissociated into anionic species in the soil solution, whose pH value is usually higher than 4.

With respect to the octanol–water partition coefficient (K_{OW}) of PFASs, literature values show considerable variability, due to the fact that the determination of this parameter for hydrophobic organic compounds is highly operational (Linkov et al., 2005). Here, the values of Deng et al. (2012) are considered for the interpretation of results. Comparing PFOS and PFOA, they contain equal number of carbon atoms in the molecule, but PFOS has more C–F units than PFOA, which has a carboxyl group. As a consequence, PFOS is more hydrophobic than PFOA. In the same way, PFBS, which has the shortest perfluorinated chain, is the compound that shows the lowest hydrophobicity.

Stock standard solutions of PFOS, PFOA and PFBS of 1 g L^{-1} were prepared individually in acetonitrile. Working solutions of PFASs for the sorption experiments were prepared by dilution of stock standards in acetonitrile. All solutions were stored at -18 °C in 20 mL glass vials with polyethylene caps (Sigma-Aldrich, Germany).

Isotopically labelled standard solutions of sodium perfluoro-1-[1,2,3,4,-^{13}C$_4$]-octane sulfonate (MPFOS) and perfluoro-n-[1,2,3,4,-^{13}C$_4$]-octanoic acid (MPFOA), both at concentrations of 50 μg mL^{-1}, were purchased from Wellington Laboratories (Canada). Working solutions of MPFOS and MPFOA were prepared by 50-times dilution of standard solutions in acetonitrile. The solutions were stored at -18 °C in chromatographic vials of 2 mL (Waters, USA).

2.2. Sample characterisation

Six soil samples with contrasting characteristics, especially in relation to the organic matter content, were selected from an already existing soil collection. ASCO, ALM, GOLOSO, DELTA2, and OVI01 were natural and agricultural soils originated from the Iberian Peninsula collected in a sampling campaign carried out in a previous work (Gil-García et al., 2008). The sixth soil, DUBLIN, was a peat soil originated from a wet meadow of Belarus. All soils corresponded to the top layer (0–10 cm depth) of plain soils. Soil samples were air-dried and sieved through a 2 mm mesh. Prior to analysis, samples were homogenised with a roller table and stored at room temperature. A summary of the main soil parameters is shown in Table 2.

Main soil parameters were previously determined as already described elsewhere (Gil-García et al., 2008). Briefly, the pH of the soil samples was measured in Milli-Q water, using a solution-to-soil ratio of 2.5 mL g^{-1}. The cation exchange capacity (CEC) was determined from the sum of the extractable bases (Ca + Mg + K + Na) plus the extractable acidity obtained by displacement with BaCl$_2$–triethanolamine (TEA) solution buffered at pH 8.2 (Burt, 2004). The particle size distribution was determined by the pipette method, based on the varying settling velocity in a fluid medium according to the particle size (Burt, 2004). Organic carbon (OC) was determined using a Thermo EA 1108 elemental analyser (Thermo Scientific, Milan, Italy). Samples were pre-treated with 2 mol L^{-1} HCl in order to eliminate carbonates, and then analysed in tin capsules using V$_2$O$_5$ as additive (ISO, 1995). The carbonate content was determined by using the calcimeter Bernard method (Mueller and Gastner, 1971).

The dissolved organic carbon (DOC) was measured in the solutions obtained by equilibration of soil samples with 0.01 mol L^{-1} CaCl$_2$ (10 mL g^{-1}). A total organic carbon analyser TOC-5000A (Shimadzu, Tokyo, Japan) was used, with previous acidification of solutions to pH 3 with HCl to remove carbonates.

Table 1

Physicochemical properties of selected PFASs.

PFC name (molecular formula)	Abbreviation	Molecular weight (g mol^{-1})	Water solubility (g L^{-1})[a]	pK_a[a]	log K_{OW}[a]
Perfluorooctane sulfonic acid (C$_8$HF$_{17}$SO$_3$)	PFOS	500.1	0.57	-3.3	5.26
Perfluorooctanoic acid (C$_8$HF$_{15}$O$_2$)	PFOA	414.0	3.4	-0.2	4.59
Perfluorobutane sulfonic acid (C$_4$HF$_9$SO$_3$)	PFBS	300.1	46.2	0.1	2.73

[a] Deng et al. (2012).

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Table 2
Main soil characteristics.

Soil	pH	CEC $(cmol_c\ kg^{-1})$	CaCO$_3$ (%)	OC (%)	DOC $(mg\ kg^{-1})$	$\dfrac{DOC^a}{OC}$	Clay (% wrt mineral content)	Sand
ASCO	8.0	42.8	38	0.2	180	0.09	17.2	18.9
ALM	5.9	23.4	2	1.6	450	0.03	10.9	56.4
GOLOSO	6.3	72.4	4	3.9	570	0.01	10.4	78.0
DELTA2	7.9	89.3	51	7.7	780	0.01	43.6	15.8
OVI01	4.6	46.3	3	9.4	5740	0.06	23.6	51.7
DUBLIN	5.3	130	2	39	7250	0.02	nd	nd

nd – not determined.
[a] DOC (%)/OC (%).

2.3. Sorption and desorption experiments

Three grams of soil was suspended in an 80 mL polypropylene centrifuge tube with 30 mL of 0.01 mol L^{-1} CaCl$_2$ solution (OECD, 2000). Additionally, 0.03 g of NaN$_3$ was added in order to suppress microbial activity and inhibit biodegradation of the target compounds, as this process might be an artefact affecting sorption experiments (Rozycki and Bartha, 1981). The resulting suspension was end-over-end shaken for 24 h, and then known volumes of the PFOS, PFOA or PFBS working solutions were added to the soil suspensions to cover a range of initial concentrations in the solutions from 5 to 1000 ng mL^{-1} for PFOS; 1 to 300 ng mL^{-1} for PFOA; and 1 to 150 ng mL^{-1} for PFBS. Due to the varying physicochemical properties of the target PFASs (Table 1), different ranges of initial concentrations were used to guarantee that there were quantifiable concentrations in the solutions at equilibrium. The resulting suspensions were further shaken for 24 h at 60 rpm and centrifuged for 30 min at 9000 g. The supernatants were then decanted off. For the subsequent desorption experiments, some of the soil residues resulting from the sorption experiments were dried at 40 °C for 48 h and then, 30 mL of 0.01 mol L^{-1} CaCl$_2$ and 0.03 g of NaN$_3$ were added to the dried soil residue and, after shaking for 24 h, the resulting suspension was centrifuged and the supernatant decanted off, as in the sorption test.

For the quantification of the target PFASs, aliquots of 750 μL of supernatants, obtained from either the sorption or the desorption experiments, were transferred into chromatography vials of 2 mL. Then, 10 μL of the 1 μg mL^{-1} working solution of the internal standard (MPFOS or MPFOA), and 240 μL of acetonitrile were added to the vial, and the analysis of PFASs was performed by ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS).

2.4. UPLC–MS/MS analysis of PFOS, PFOA and PFBS

The system consisted of an Acquity UPLC (Waters, Milford, Massachusetts, USA) connected to a Triple Quadruple Detector. An Eclipse XDB-C18 column (150 × 2.1 mm, 5 μm particle size) (Agilent, Santa Clara, California, USA) was connected to a C18 pre-column.

Chromatographic separation conditions were adapted from Gómez-Canela et al. (2012). In short, a binary gradient mobile phase consisting of acetonitrile (A) and 3 mM ammonium acetate (B) was used for the analysis. Gradient elution started at 25% of A and 75% of B for 1 min, increased to 85% of A in 5 min, and then to 100% of A in 30 s, which was then maintained for 30 s. Initial conditions were achieved again in the next 1 min, and the system was stabilised for 4 min. The flow rate was set at 0.3 mL min^{-1} and the injection volume was 10 μL. The main working parameters for the MS detector were set as follows: capillary voltage of 2.8 kV, cone gas flow of 50 L h^{-1}, desolvation gas flow of 100 L h^{-1}, source temperature of 120 °C, and desolvation temperature of 400 °C. Nitrogen (99.9%) and argon (99.9%) were used as cone and collision gases, respectively.

The analysis of PFASs was performed in negative electrospray ionisation mode, and compounds were identified using their characteristic quantification transitions from precursor to product ions and their retention times (Fig. S1 in the Supplementary information). Two peaks were observed for PFOS. The one with the higher retention time was attributed to the most abundant and hydrophobic linear form; and the other was attributed to branched isomers (Langlois and Oehme, 2006). The cone voltages and collision energies of multiple reactions used for the analysis of MPFOS, PFOS, MPFOA, PFOA and PFBS were 52, 50, 17, 19 and 50 V and 39, 42, 10, 11 and 29 eV, respectively. The dwell time established for each transition was 0.1 s and the interscan delay was set at 10 ms.

Quantification was based on a seven-point calibration curve with a PFAS concentration range from 1 to 200 ng mL^{-1}. Regression coefficients were always higher than 0.99. MPFOS was used as an internal standard for the quantification of PFOS, and MPFOA was used for the quantification of PFOA and PFBS. The detection limits of the method (LOD$_{method}$) were determined for each PFAS as the concentration with a signal-to-noise ratio of three. The values, expressed with respect to the solution obtained from sorption experiments, were: 0.1 ng mL^{-1} for PFOS and PFOA, and 0.3 ng mL^{-1} for PFBS.

2.5. Quality control

To minimise the contamination of samples, Teflon (polytetrafluoroethylene) material was not used in the experiments. Blanks of samples were run in parallel to check that the soil samples did not contribute to the concentration of target compounds measured in the supernatants. Furthermore, control tests were run in the same tubes and conditions as in the sorption tests (using 70 ng mL^{-1} PFOS, 40 ng mL^{-1} PFOA, 70 ng mL^{-1} PFBS, 1.7 ng mL^{-1} MPFOS, and 1.7 ng mL^{-1} MPFOA). The results showed that there were no significant compound losses due to PFAS sorption on the material used or degradation. The reproducibility of the method, calculated as the relative standard deviation of triplicate analyses of samples was reasonable in the range of 5–15%.

2.6. Quantification of sorption and desorption parameters

The solid–liquid distribution coefficient of the sorption, K_d (mL g^{-1}), was calculated as the ratio between the concentration of the target compound (PFOS, PFOA or PFBS) sorbed in the soil, C_s (ng g^{-1}), and its concentration in the aqueous phase at equilibrium, C_{eq} (ng mL^{-1}):

$$K_d = \frac{C_s}{C_{eq}} \tag{1}$$

C_{eq} values were directly determined by UPLC–MS/MS and the corresponding concentrations of PFASs sorbed by soil, whereas C_s was calculated by the following equation:

$$C_s = \frac{\left(C_{in} - C_{eq}\right) \cdot V}{m_{soil}} \tag{2}$$

where C_{in} (ng mL^{-1}) corresponds to the initial concentration of PFAS added to the soil suspension, V (mL) is the volume of solution and m_{soil} (g) refers to the dry mass of the soil sample.

Moreover, the percentage of sorbed PFAS, S (%) was calculated according to the following equation:

$$S(\%) = \frac{C_s \cdot m_{soil}}{C_{in} \cdot V} \cdot 100 \tag{3}$$

The sorption reversibility was evaluated through the desorption yield, D (%), which was calculated from the ratio between the amount of PFAS desorbed and the amount present in the soil prior to the desorption experiment, as follows:

$$D(\%) = \frac{C_{eq,des} \cdot V}{C_{in,des} \cdot m_{soil}} \cdot 100 \tag{4}$$

where $C_{eq,des}$ (ng mL^{-1}) is the concentration of PFAS found in the liquid phase after the desorption experiment, V (mL) is the volume of solution used in the desorption experiment, m_{soil} (g) refers to the dry mass of soil residue resulting from the sorption experiment, and $C_{in,des}$ (ng g^{-1}) is the initial concentration of PFAS in this residue, which can be taken as C_s. However, if required for better quantification of $C_{in,des}$, C_s can be corrected by the amount of PFAS present in the residual volume of solution ($C_{eq} \cdot V_{res}$) that remained in the soil after the sorption experiment:

$$C_{in,des} = C_s + \frac{C_{eq} \cdot V_{res}}{m_{soil}} \tag{5}$$

2.7. Fitting of sorption isotherms

Sorption isotherms were constructed by plotting C_s vs. C_{eq} for each PFAS–soil combination. They were fitted to the Freundlich and linear models, which are the most frequently used for hydrophobic compounds (Hinz, 2001) and have been previously used for describing PFAS sorption in sediments (Higgins and Luthy, 2006; Ahrens et al., 2011; Zareitalabad et al., 2013). Additional representations of K_d vs. C_s were also useful to decide on the most appropriate model to fit the isotherms (Hinz, 2001).

The Freundlich model is quantitatively described by the following equation:

$$C_s = K_F \cdot \left(C_{eq}\right)^N \tag{6}$$

where K_F, whose units depend on N values, is the Freundlich constant, which expresses the affinity of a compound to a given solid sorbent, here the soil sample, and N is a dimensionless empirical parameter that describes the degree of isotherm non-linearity. For $N < 1$, the sorption isotherm is convex and the K_d value decreases with C_s, whereas for $N > 1$, the Freundlich isotherm is characterised by a concave shape, and the values of K_d increase with C_s. When N is approximately equal to 1, the Freundlich model can be considered linear. In this case, the value of K_F approaches the value of K_d that is valid for the entire concentration range tested.

The K_F and N parameters of the Freundlich equation were calculated by non-linear least squares fitting of the sorption isotherms. The Solver function of Microsoft Excel™ spreadsheet was used in order to find the set of adjustable parameters that minimized the root mean square error (RMSE), which for m experimental data points and p adjustable fitting parameters is calculated as (Kinniburgh, 1986; Teixidó et al., 2012):

$$RMSE = \left(\frac{RSS}{m-p}\right)^{\frac{1}{2}} \tag{7}$$

where RSS is the weighted residual sum of squares, which for m experimental data is given by the following equation:

$$RSS = \sum_{i=1}^{m} \frac{\left(C_{s,exp,i} - C_{s,cal,i}\right)^2}{\left(C_{s,cal,i}\right)^2} \tag{8}$$

where $C_{s,exp,i}$ and $C_{s,cal,i}$ are the experimental and calculated sorbed concentrations, respectively. The use of weighted non-linear least squares offers the possibility for all data points to be equally weighted in the model. The standard error of the N and K_F parameters was calculated with the macro-Solvstat.xls for Microsoft Excel™.

Sorption isotherms could also be fitted to a linear equation in most cases, described by a constant slope of C_s vs. C_{eq} in the entire concentration range investigated. In this case, the best estimated K_d value, which was valid for the entire tested concentration range ($K_{d,linear}$), was deduced directly from the slope of the isotherm.

3. Results and discussion

3.1. Soil characteristics

The main physicochemical characteristics of the soils studied here are summarised in Table 2. Particle size analysis was carried out for all soils, except for DUBLIN (which had extremely high organic matter content), and showed that the clay content varied from 10% in ASCO to 44% in DELTA2. According to the United States Department of Agriculture (USDA) criteria, ASCO soil had a silt loamy texture, ALM and GOLOSO soils, with varying OC, were sandy loam soils, whereas DELTA2 and OVI01 soils, with higher OC, were clay loamy and loam soils, respectively. Soil DUBLIN with an OC content of 39% can be classified as organic soil.

Several soils were acidic (ALM, GOLOSO, OVI01 and DUBLIN) and had CaCO$_3$ content lower than 4%. In contrast, ASCO and DELTA2 soils were basic and presented a high content of CaCO$_3$. The content of organic carbon varied more than two orders of magnitude (from 0.2 in the ASCO soil up to 39% in DUBLIN), and the DOC content increased with OC with maximum values for OVI01 and DUBLIN. As shown in Table 2, ratios of DOC vs. OC were also calculated in order to verify whether differences in the quality of the organic matter affecting its water solubility might help in the interpretation of sorption mechanisms. The highest DOC/OC ratio was found in the ASCO soil, which had the lowest OC content but the highest pH. Despite the low pH of the OVI01 soil, the OC content was relatively soluble and its DOC/OC ratio was the second highest among the soils investigated. For the rest of the soils, similar DOC/OC ratios were obtained.

3.2. Sorption behaviour of PFOS, PFOA and PFBS

3.2.1. Description of sorption isotherms

The sorption isotherms of PFOS in the soils are shown in Fig. 1, whereas the sorption isotherms of PFOA and PFBS are shown in Fig. 2. The sorption pattern of C_s vs. C_{eq} was considerably linear for all PFAS–soil combinations at the concentration ranges studied, which was also confirmed by the nearly constant K_d values as a function of changes in C_s (Figs. S2–S4 in the Supplementary information). The almost constant partitioning of the three PFASs is also evidenced, in Table 3, by the similar values of $K_{d,min}$ and $K_{d,max}$ for the same PFAS–soil combination, with a difference of a factor of two in most cases. In contrast, K_d differences were higher between PFASs. Of the studied PFASs, PFOS showed the highest K_d values. The values for PFOA and PFBS were considerably lower. The sequence of K_d values for the three PFASs was in agreement with the respective physico-chemical properties. Thus, PFOS with the lowest water solubility and the highest hydrophobicity (Table 1) showed the highest K_d values (from 9–22 mL g^{-1} for ASCO to 243–444 mL g^{-1} for DUBLIN),
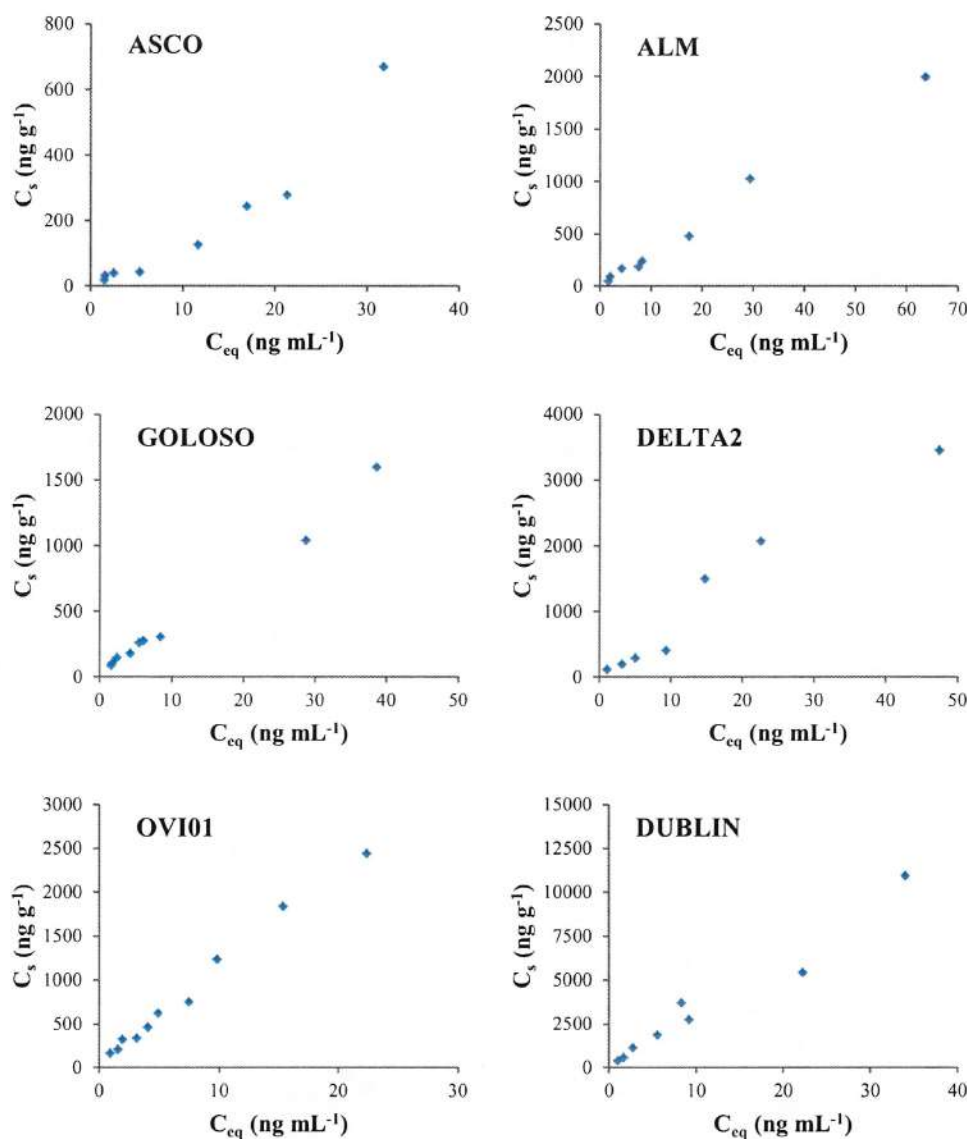
Fig. 1. Sorption isotherms of PFOS in the analysed soils.

whereas PFOA and PFBS showed K_d values below 49 mL g^{-1} and 8 mL g^{-1}, respectively. The higher sorption of PFOS than PFOA can be explained by the presence of an additional C–F unit in the perfluorinated chain (Zhou et al., 2010). Furthermore, PFBS had lower K_d values than PFOS due to its much shorter perfluorinated carbon chain and, consequently, lower hydrophobicity and higher water solubility. When a given PFAS was considered, K_d values rose when the organic matter in the soil increased. This suggested that the main sorption mechanism of PFASs is based predominantly on interactions between the hydrophobic C–F chain of PFAS and the soil organic matter, as indicated in previous works (Ahrens et al., 2010; Dai et al., 2013; Zareitalabad et al., 2013).

The sorption percentages of PFOS in soils were in a broad range (from 46 to 97%) and systematically increased with the OC content of the soil (Table 3), in the same way as the K_d values. In contrast, the sorption percentages of PFOA and PFBS were much lower, from 7 to 81% and from 1 to 40%, respectively, and were only significant for those soils with a higher organic matter content, such as OVI01 and DUBLIN, indicating that the hydrophobic interaction plays a key role in the sorption of PFASs in soils.

3.2.2. Fitting of sorption isotherms

In order to confirm the linearity of C_s vs. C_{eq} and to deduce a best-estimate K_d value for each PFAS–soil combination, the sorption isotherms were fitted to the Freundlich and linear models. The exception was PFBS in ASCO and ALM soils, which had extremely low sorption that made it difficult to obtain good quality data. In these two cases, the small amount of data only allowed us to derive a K_d value from the linear model. Table 3 shows the values of the N and K_F parameters obtained from the Freundlich fitting, as well as the $K_{d,linear}$ values derived from the slope of the C_s vs. C_{eq} correlation. In all cases, satisfactory fitting was obtained with $R^2 > 0.92$. Values of N obtained from the Freundlich fitting were close to 1 for all PFAS–soil combinations, which confirms the constant partitioning of the three PFASs in all soils. Moreover, although the standard error associated with K_F was considerably higher to that obtained for $K_{d,linear}$, the two parameters were well correlated for the three PFASs in soils ($K_F = 1.3\,(0.1) \cdot K_{d,linear}$; $R_2 = 0.99$). According to Karickhoff (1981), sorption linearity can be partially explained by the fact that C_{eq} values of PFASs, at the environmental levels considered in the present study, were below one half their solubility in water (values shown in Table 1). The linearity of

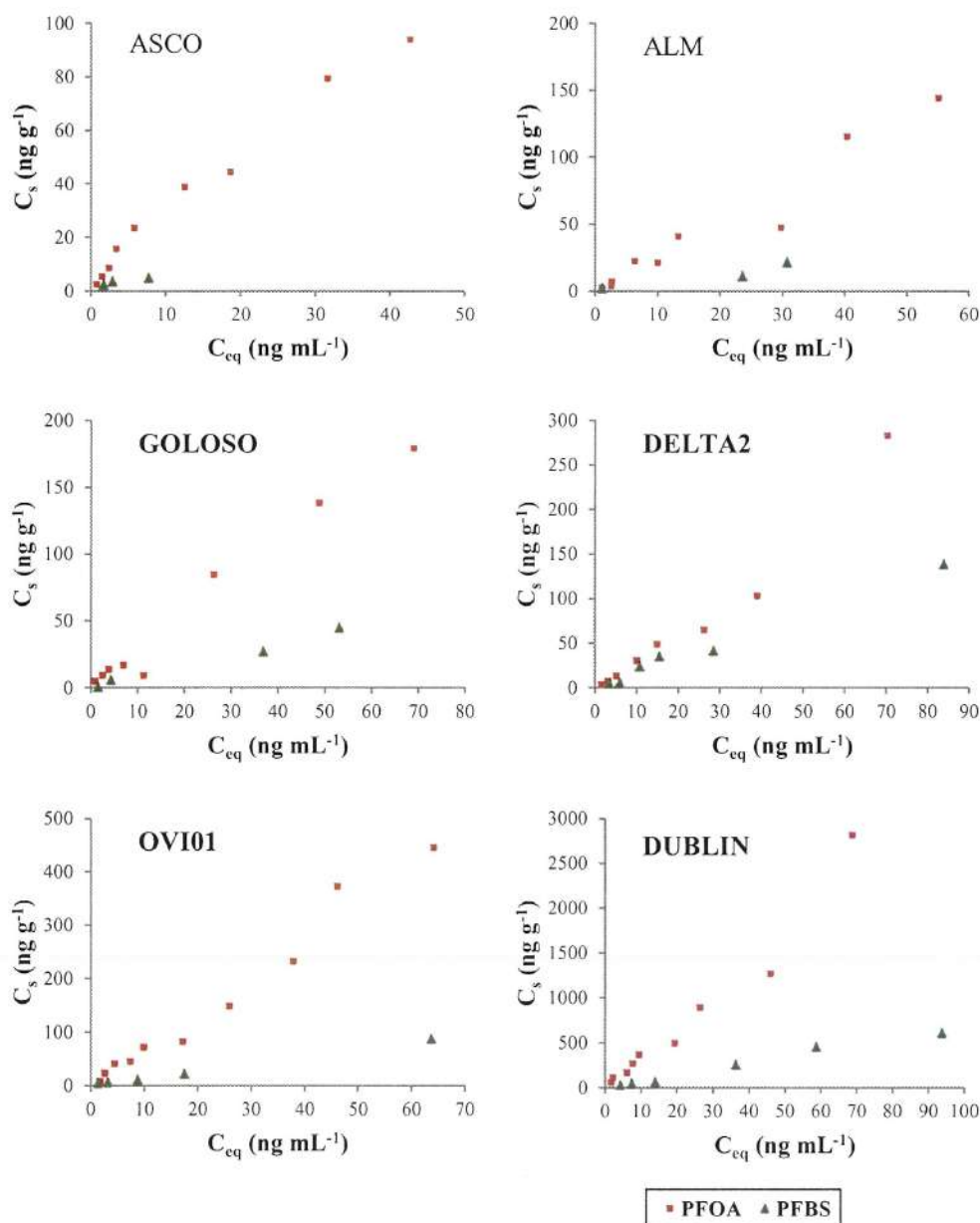J. Milinovic et al. / Science of the Total Environment 511 (2015) 63–71

Fig. 2. Sorption isotherms of PFOA and PFBS in the analysed soils.

sorption isotherms also agreed with previously reported results for PFASs (Enevoldsen and Juhler, 2010; Chen et al., 2013).

The $K_{d,linear}$ data obtained in this study for PFOS were in good agreement with previous works, in which K_d values were obtained in the range 12–17 mL g^{-1} for soil samples containing less than 1% of organic carbon (Chen et al., 2009; Enevoldsen and Juhler, 2010), which is similar to the value obtained for the ASCO sample (OC = 0.2%). Furthermore, Chen et al. (2013) also reported very similar K_d values, from 7.3 to 115 mL g^{-1}, in five soils with OC ranging from 0.5 to 16%. Regarding PFOA, the $K_{d,linear}$ values were very low in comparison with PFOS for the concentration range studied, as they ranged from 2.2 to 38 mL g^{-1}. These results are also in agreement with the K_d values reported by Chen et al. (2013), which ranged from 2.3 to 16.1 mL g^{-1} for soils with OC from 0.5 to 16%. Finally, $K_{d,linear}$ values obtained for PFBS were extremely low, from 0.4 mL g^{-1} for ASCO to 7 mL g^{-1} for DUBLIN (Table 3). The $K_{d,linear}$ obtained for ASCO agreed with the K_d value of 0.41 mL g^{-1} reported by Enevoldsen and Juhler (2010) for PFBS in a soil with 1% of OC.

3.2.3. Sorption reversibility of PFASs

The sorption reversibility of each compound in five soil samples is shown in Fig. 3. As can be seen, the lowest desorption yields were found for PFOS ($D < 13\%$), which indicates that the sorption of this compound in soils is highly irreversible. PFOA and PFBS behaved in a similar way, showing much higher desorption yields, from 24 to 58% and from 32 to 60%, respectively. Therefore, PFOS showed both the highest sorption and the lowest sorption reversibility, which can also be attributed to its lowest water solubility and highest hydrophobicity among the PFASs examined. Therefore, we confirmed the important role of hydrophobic interaction in the sorption mechanism.

3.3. Correlation of K_d with soil characteristics

As OC played a major role in the variation of the sorption parameters of PFASs in the soils investigated, we decided to further explore the relationship between the K_d and the fraction of organic carbon in soil, F_{OC} (expressed as gram of OC per gram of soil). The K_d of organic

Table 3
Sorption parameters obtained from the Freundlich and linear model for PFOS, PFOA and PFBS sorption in the analysed soils.
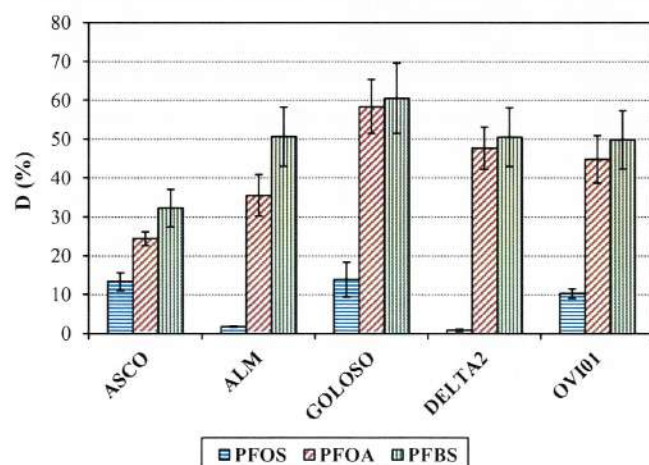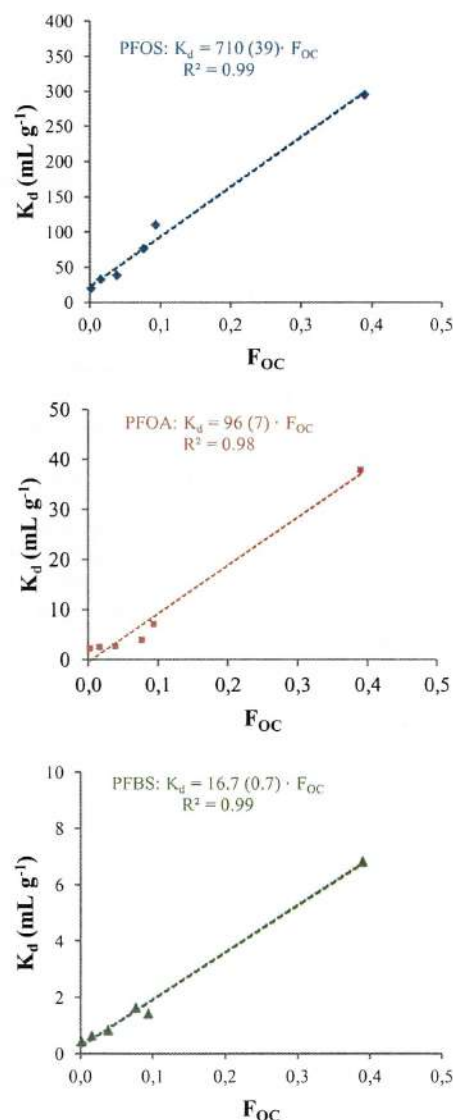
PFC	Soil	Experimental data				Freundlich		Linear
		$K_{d,min}$ (mL g^{-1})	$K_{d,max}$ (mL g^{-1})	S_{min} (%)	S_{max} (%)	N (SE)	K_F (SE) (ng$^{(1-N)}$ mL^N g^{-1})	$K_{d,linear}$ (SE) (mL g^{-1})
PFOS	ASCO	9	22	46	68	1.0 (0.1)	17 (6)	19 (2)
	ALM	25	48	71	83	0.9 (0.1)	41 (11)	32 (1)
	GOLOSO	35	63	78	86	0.9 (0.1)	61 (16)	38 (2)
	DELTA2	43	104	81	91	1.0 (0.1)	86 (38)	76 (7)
	OVI01	100	182	91	95	0.9 (0.1)	157 (23)	110 (4)
	DUBLIN	243	444	95	97	0.9 (0.1)	389 (150)	295 (25)
PFOA	ASCO	2.4	4.0	18	31	0.9 (0.1)	4 (1)	2.2 (0.1)
	ALM	1.3	3.5	11	26	1.1 (0.2)	2 (1)	2.6 (0.2)
	GOLOSO	0.8	4.3	7	30	0.9 (0.1)	4 (2)	2.7 (0.2)
	DELTA2	1.8	4.0	15	29	1.1 (0.1)	2 (1)	3.9 (0.3)
	OVI01	3.4	8.7	25	46	1.0 (0.1)	7 (3)	7.1 (0.4)
	DUBLIN	25	49	70	81	1.0 (0.2)	40 (25)	38 (3)
PFBS	ASCO	0.6	1.2	6	10	–	–	0.4 (0.1)
	ALM	0.4	1.2	4	11	–	–	0.6 (0.2)
	GOLOSO	0.1	1.2	1	11	0.9 (0.2)	1.3 (0.9)	0.8 (0.1)
	DELTA2	0.8	2.2	8	18	1.0 (0.1)	1.8 (0.6)	1.6 (0.1)
	OVI01	1.2	3	10	23	1.0 (0.1)	1.1 (0.3)	1.4 (0.1)
	DUBLIN	4	8	28	40	1.1 (0.1)	5 (3)	6.8 (0.4)

SE: standard error.

compounds in soils can be expressed as the sum of two contributions: the $K_{d,MIN}$ that describes the sorption of the compound on the mineral fraction of soil, basically attributed to the hydrophilic part of the molecule; and the $K_{d,ORG}$ that would correspond to hydrophobic interaction with the organic matter fraction:

$$K_d = K_{d,ORG} + K_{d,MIN} = K_{OC} \cdot F_{OC} + K_{d,MIN} \tag{9}$$

where $K_{d,ORG}$ can be expressed as the product of the solid–liquid distribution coefficient of the compound in the organic fraction (referred to the weight of organic carbon), K_{OC}, and the fraction of organic carbon in the soil, F_{OC}, expressed as grams of organic carbon per gram of soil. Therefore, a K_{OC} value for a given PFAS can be derived from the slope of the K_d vs. F_{OC} correlation obtained in various soils. Fig. 4 plots the correlations obtained for the three PFASs investigated in this study. The strong dependence between the K_d values and the soil organic carbon for PFOS, PFOA and PFBS ($R^2 = 0.99$, 0.98 and 0.99, respectively) allowed us to deduce K_{OC} values from the slope of the curves. We found that PFOS ($K_{OC} = 710$ (39) mL g^{-1}) had higher sorption in organic matter than PFOA ($K_{OC} = 96$ (7) mL g^{-1}) and PFBS ($K_{OC} = 16.7$ (0.7) mL g^{-1}). The values for the intercepts ($K_{d,MIN}$) were not statistically

Fig. 3. Desorption yield (%) of PFOS, PFOA and PFBS in five soils.

Fig. 4. $K_{d,linear}$ as a function of the fraction of organic carbon for PFOS, PFOA and PFBS.

different to zero, which indicates that the soil mineral fraction has a negligible role in the sorption pattern of the three compounds. This was consistent with the proposed sorption mechanism. The deduced log K_{OC} values for PFOS (2.9) and PFOA (2.0) were close to the reported values of 2.8–3.2 for PFOS and 2.0–2.6 for PFOA from similar experiments (Chen et al., 2013), but lower than the reported values of 3.1–3.6 for PFOS (Chen et al., 2009) and 2.2–2.6 for PFOA (Enevoldsen and Juhler, 2010), corresponding to soils with a very low OC content (<1%). The log K_{OC} for PFBS (1.2) was similar to the reported values of 1.2–1.6 obtained by Enevoldsen and Juhler (2010).

Although individual K_{OC} values could be obtained for each soil, a K_{OC} derived from the correlation would be more representative of a series of soils with a broad range of OC content, as is the case of the present study, because soils with an extremely low OC content might lead to overestimation of the K_{OC} value. A recent review by Zareitalabad et al. (2013) helps to corroborate the fact that the K_{OC} obtained from sorption experiments, in spite of being a sorption parameter normalized to the organic matter content, presents a high variability as a function of the nature of the type of solid phase considered. In this sense, the K_{OC} values obtained in this work for a series of soils with a very different origin and composition, agreed with the mean value reported for different matrices and experimental conditions (Zareitalabad et al., 2013), with log K_{OC} within the 2.8–3.0 range for PFOS and 2.1 for PFOA.

3.4. Correlation of K_d with physicochemical properties of PFASs

As mentioned before, PFOS showed higher sorption than PFOA and PFBS in soils. The same sequence of sorption (PFOS > PFOA > PFBS) was obtained elsewhere (Enevoldsen and Juhler, 2010). As already pointed out, the different affinities of the selected PFASs for soils may be attributed to the varying hydrophobicity derived from their structure, including both the length of the perfluorinated carbon chain and the functional hydrophilic group. For the three PFASs studied here, a good correlation was obtained between the log K_{OC} and the log K_{OW} values (log K_{OC} = 0.6 (0.2) · log K_{OW}; R^2 = 0.91), which confirmed that not only the soil characteristics (basically the organic matter content), but also the physicochemical properties of PFASs influenced their sorption pattern in soils.

K_d values for PFOS and PFBS were also well-correlated (K_d (PFOS) = 42 (4) · K_d (PFBS); R^2 = 0.97), which provided information about the influence of the length of the perfluorinated carbon chain on the sorption of PFASs in soils. Based on the difference between the log K_{OC} values of PFOS and PFBS (1.6 log units), we can suggest that each CF_2 moiety increased the log K_{OC} value by about 0.4 log units. This value cannot be compared with previous results, due to the lack of available information on the impact of CF_2 moiety in soils. Nevertheless, a similar value of 0.55 log units has been reported in similar environmental matrices, such as sediments (Higgins and Luthy, 2006).

4. Conclusions

Sorption of PFOS, PFOA and PFBS in soils was linear and depended not only on the soil characteristics, but also on the physicochemical properties of the studied compounds. The present study confirmed that the sequence of affinity of PFASs in soils is PFOS > PFOA > PFBS. Moreover, sorption of PFOS was highly irreversible, whereas PFOA and PFBS showed higher sorption reversibility. The main sorption process of PFASs was attributed to a hydrophobic interaction between the perfluorinated carbon chain and the organic matter of soil, as indicated by the correlation between the solid–liquid distribution coefficient and the fraction of organic carbon.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2014.12.017.

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